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(54) 【発明の名称】 水性顔料分散体の製造方法

(57) 【要約】

【課題】 保存安定性、耐水性、耐溶剤性に優れた水性顔料分散体を製造する。

【解決手段】 (1) 顔料を、界面活性剤および(または)水可溶性樹脂を用いて予め水媒体に分散させる第1工程、(2) 第1工程で得られた分散液と重量平均分子量が3000~100000の範囲にある自己乳化型樹脂を水溶性溶剤に溶解させた液とを混合し、顔料表面に自己乳化型樹脂を固着させる第2工程により水性顔料分散体を製造する。

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【特許請求の範囲】

【請求項 1】 (1) 顔料を、界面活性剤および（または）水可溶性樹脂を用いて予め水媒体に分散させる第 1 工程、(2) 第 1 工程で得られた分散液と重量平均分子量が 3000～100000 の範囲にある自己乳化型樹脂を水溶性溶剤に溶解させた液とを混合し、顔料表面に自己乳化型樹脂を固着させる第 2 工程からなる水性顔料分散体の製造方法。

【請求項 2】 (1) 顔料を、界面活性剤および（または）水可溶性樹脂を用いて予め水媒体に分散させる第 1 工程、(2) 第 1 工程で得られた分散液と重量平均分子量が 3000～100000 の範囲にある自己乳化型樹脂および架橋剤を水溶性溶剤に溶解させた液とを混合し、顔料表面に自己乳化型樹脂および架橋剤を固着させる第 2 工程からなる水性顔料分散体の製造方法。

【請求項 3】 前記界面活性剤が、非イオン性界面活性剤および（または）陰イオン性界面活性剤である請求項 1 または 2 記載の製造方法。

【請求項 4】 前記水可溶性樹脂が、分子中にカルボキシル基およびスルホン酸基の少なくとも 1 種の親水性基を有し、スチレン単位および（または）メチルスチレン単位を 50 重量%以上含有する重量平均分子量が 2000～20000 の重合体である請求項 1 または 2 記載の製造方法。

【請求項 5】 前記自己乳化型樹脂が、ウレタン系樹脂またはアクリル系樹脂である請求項 1 または 2 記載の製造方法。

【請求項 6】 前記自己乳化型樹脂の酸価が 20～110 の範囲にある請求項 1、2 または 5 記載の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、水性塗料、水性インキや捺染、またはカラーフィルターやインクジェット用トナーなどに有用な水性顔料分散体の製造方法に関する。

【0002】

【従来の技術および発明が解決しようとする課題】従来から、顔料分散体は、塗料、印刷インキ、筆記用具インキ、捺染などの用途に幅広く用いられてきている。そして、近年では、インクジェット用やカラーフィルター用に用途が拡大されつつあり、そのために顔料分散体の性能向上が要求されている。

【0003】水性の顔料分散体は、一般に非イオンの作用あるいはイオンの作用によって安定化される。

【0004】非イオンの作用によって安定化させる非イオン性界面活性剤または水溶性樹脂は、疎水性部分が顔料と吸着し、親水性部分が水中に伸展してエントロピー的または立体的に、顔料粒子間の再凝集を防止する。

【0005】また、イオンの作用によって安定化させる陽イオン性界面活性剤、陰イオン性界面活性剤または中

和型樹脂の場合は、まずイオン化することにより親水性が現れる部分が水中に伸展して、顔料粒子の周囲に電気二重層を形成する。そして、この電気二重層が電氣的反発力を生み、顔料粒子間の再凝集を防止する。

【0006】このような安定化機構によって分散されている水性顔料分散体は、用途によりいろいろな問題が現れてくる。たとえば、界面活性剤を用いて分散された顔料分散体を使用した塗料は、得られる塗膜の耐水性がわるいという問題がある。また、一般の顔料分散体は、顔料と分散剤が吸着という弱い結合のみで引き合っているため、水媒体中の極性変化に弱い、つまり耐溶剤性が弱いという問題がある。

【0007】本発明は、前記従来技術に鑑みてなされたものであり、微粒子で保存安定性、耐水性、耐溶剤性に優れた水性顔料分散体の製造方法を提供することを目的とする。

【0008】

【課題を解決するための手段】本発明者らは、微粒子で保存安定性、耐水性、耐溶剤性に優れた水性顔料分散体を得るべく鋭意検討を重ねた結果、本発明を完成するに至った。

【0009】すなわち、本発明は、(1) 顔料を、界面活性剤および（または）水可溶性樹脂を用いて予め水媒体に分散させる第 1 工程、(2) 第 1 工程で得られた分散液と重量平均分子量が 3000～100000 の範囲にある自己乳化型樹脂を水溶性溶剤に溶解させた液とを混合し、顔料表面に自己乳化型樹脂を固着させる第 2 工程からなる水性顔料分散体の製造方法（請求項 1）、

(1) 顔料を、界面活性剤および（または）水可溶性樹脂を用いて予め水媒体に分散させる第 1 工程、(2) 第 1 工程で得られた分散液と重量平均分子量が 3000～100000 の範囲にある自己乳化型樹脂および架橋剤を水溶性溶剤に溶解させた液とを混合し、顔料表面に自己乳化型樹脂および架橋剤を固着させる第 2 工程からなる水性顔料分散体の製造方法（請求項 2）、前記界面活性剤が、非イオン性界面活性剤および（または）陰イオン性界面活性剤である請求項 1 または 2 記載の製造方法（請求項 3）、前記水可溶性樹脂が、分子中にカルボキシル基およびスルホン酸基の少なくとも 1 種の親水性基を有し、スチレン単位および（または）メチルスチレン単位を 50 重量%（以下、%という）以上含有する重量平均分子量が 2000～20000 の重合体である請求項 1 または 2 記載の製造方法（請求項 4）、前記自己乳化型樹脂が、ウレタン系樹脂またはアクリル系樹脂である請求項 1 または 2 記載の製造方法（請求項 5）、および前記自己乳化型樹脂の酸価が 20～110 の範囲にある請求項 1、2 または 5 記載の製造方法（請求項 6）に関する。

【0010】

【発明の実施の形態】本発明では、まず、第 1 工程とし

て、顔料が、界面活性剤および（または）水可溶性樹脂を用いて予め水媒体に分散せしめられる。このとき、必要であればその他の添加剤も予め添加しておいてもよい。

【0011】前記顔料にはとくに限定はなく、たとえばアゾレーキ、不溶性アゾ顔料、縮合アゾ顔料、キレートアゾ顔料などのアゾ顔料類；フタロシアニン顔料、ペリレン顔料、チオインジゴ顔料、イソインドリノン顔料、キノフタロン顔料などの多環式顔料類；染料キレートなどの各種有機顔料や、酸化チタン、ベンガラ、酸化クロム、鉄黒などの酸化物；カドミウムイエロー、クロムバーミリオン、紺青、群青、黄色酸化鉄などの各種無機顔料や、カーボンブラックなどがあげられる。これらは単独で用いてもよく、2種以上を組み合わせ用いてもよい。

【0012】前記有機顔料の具体例としては、たとえばピグメント・イエロー1 (C.I. 11680)、ピグメント・イエロー3 (C.I. 11710)、ピグメント・イエロー74 (C.I. 11741)、ピグメント・イエロー83 (C.I. 21108)、ピグメント・イエロー106、ピグメント・イエロー108 (C.I. 68240)、ピグメント・イエロー117、ピグメント・イエロー126、ピグメント・イエロー139、ピグメント・イエロー185、ピグメント・オレンジ5 (C.I. 12075)、ピグメント・オレンジ67、ピグメント・レッド3 (C.I. 12120)、ピグメント・レッド22 (C.I. 12315)、ピグメント・レッド48:1 (C.I. 15865:1)、ピグメント・レッド48:4 (C.I. 15865:4)、ピグメント・レッド101 (C.I. 77491)、ピグメント・レッド112 (C.I. 12370)、ピグメント・レッド123 (C.I. 71145)、ピグメント・レッド169 (C.I. 45160:2)、ピグメント・バイオレット23 (C.I. 51319)、ピグメント・バイオレット27 (C.I. 42555:3)、ピグメント・ブルー1 (C.I. 42595:3)、ピグメント・ブルー15:1 (C.I. 74160)、ピグメント・ブルー15:3 (C.I. 74160)、ピグメント・ブルー15:6 (C.I. 74160)、ピグメント・ブルー61 (C.I. 42765:1)、ピグメント・グリーン7 (C.I. 74260)、ピグメント・グリーン36 (C.I. 74265)などがあげられる。

【0013】また、前記無機顔料の具体例として、たとえばピグメント・イエロー42 (C.I. 77492)、ピグメント・ホワイト6 (C.I. 77981)、ピグメント・ブルー27 (C.I. 77510)、ピグメント・ブルー29 (C.I. 77007)、ピグメント・ブラック7 (C.I. 77266)などがあげられる。

【0014】なお、前記顔料の形態にはとくに限定がなく、各種表面処理を施したもの、粉体、水性ペーストなどのいずれであってもよい。これらは単独で用いてもよく、2以上種を組み合わせ用いてもよい。これらのうちでは分散性が良好であるという点から水性ペーストが

好ましい。

【0015】また、前記顔料の1次粒子径は、分散性を考慮すると、通常0.1 μm 程度以下、なかんづく0.01~0.06 μm であるのが好ましい。

【0016】前記顔料の配合量にはとくに限定はないが、十分な着色力を得るためには、第1工程で得られる分散液における濃度が1%以上、なかんづく3%以上になるように調整するのが好ましく、また分散液の粘度が高すぎると、第2工程で水溶性溶剤と混合する際に拡散速度が遅くなり、粒子径が大きくなる原因になるので、80%以下、なかんづく40%以下となるように調整するのが好ましい。

【0017】前記界面活性剤および（または）水可溶性樹脂としては従来から用いられてきているものである限りとくに限定はない。たとえば陽イオン性界面活性剤、陰イオン性界面活性剤、非イオン性界面活性剤などの界面活性剤や、水溶性アクリル系樹脂、水溶性ナイロン系樹脂、水溶性エポキシ系樹脂、水溶性天然高分子などの水可溶性樹脂があげられる。これらは単独で用いてもよく2種以上を組み合わせ用いてもよい。つまり、第1工程の分散までは、従来の水性顔料分散体の製法と同じであるから、従来の製造設備がそのまま使用できるメリットがある。

【0018】前記界面活性剤のうちの非イオン性界面活性剤としては、ポリオキシエチレンアルキルエーテル、ポリオキシエチレンアルキルアリールエーテル、ポリオキシエチレンオキシプロピレンブロックコポリマー、ソルビタン脂肪酸エステル、ポリオキシエチレンソルビタン脂肪酸エステル、ポリオキシエチレンソルビトール脂肪酸エステル、グリセリン脂肪酸エステル、ポリオキシエチレン脂肪酸エステル、ポリオキシエチレンアルキルアミン、フッ素系の非イオン性界面活性剤、シリコーン系の非イオン性界面活性剤などがあげられる。これらは単独で用いてもよく、2以上種を組み合わせ用いてもよい。

【0019】前記界面活性剤のうちの陰イオン性界面活性剤としては、脂肪酸塩、アルキル硫酸エステル塩、アルキルアリールスルホン酸塩、アルキルナフタレンスルホン酸塩、ジアルキルスルホン酸塩、ジアルキルスルホコハク酸塩、アルキルジアリールエーテルジスルホン酸塩、アルキルリン酸塩、ポリオキシエチレンアルキルエーテル硫酸塩、ポリオキシエチレンアルキルアリールエーテル硫酸塩、ナフタレンスルホン酸フォルマリン縮合物、ポリオキシエチレンアルキルリン酸エステル塩、グリセロールボレイト脂肪酸エステル塩などがあげられる。これらは単独で用いてもよく、2以上種を組み合わせ用いてもよい。

【0020】前記界面活性剤のうちの陽イオン性界面活性剤としては、脂肪族アミン塩、第4級アンモニウム塩、スルホニウム塩、ホスホニウム塩などがあげられ

る。これらは単独で用いてもよく、2種以上を組み合わせ用いてもよい。

【0021】前記界面活性剤の使用量にはとくに限定がないが、第1工程の分散液中における顔料の分散性を充分に向上させるには、前記顔料100重量部（以下、部という）に対して5部以上、なかんづく10部以上であるのが好ましく、また第2工程でさらに自己乳化型樹脂を添加することを考えると、分散液の粘度があがりすぎないように、かつ界面活性剤が過剰に入りすぎて品質がわるくならないようにするためには、100部以下、なかんづく50部以下であるのが好ましい。

【0022】前記水可溶性樹脂は、顔料を分散させるために用いられるものであり、その種類にはとくに限定はないが、顔料に吸着する疎水基と水媒体中に展開する親水基のバランスをよくして水可溶性樹脂の分散効果を高め、分散性を向上させるという点から、たとえばスチレン単位、メチルスチレン単位などの疎水性モノマー単位、好ましくはスチレン単位および（または）メチルスチレン単位を50%以上、さらには50～70%、なかんづく55～70%の水可溶性樹脂が好ましい。また、かかる水可溶性樹脂の重量平均分子量は、分散性の向上を考慮すると、2000～20000、なかんづく2500～15000であるのが好ましい。

【0023】前記水可溶性樹脂としては、アルカリ性化合物で中和して水溶性を呈する酸価が110～300、さらには115～300、なかんづく150～250の樹脂をアルカリ性化合物で中和したものなどが好ましい。したがって、かかる酸価となるような量の、たとえばカルボキシル基、スルホン酸基などの親水性基の少なくとも1種を分子中に有する重合体などが好ましい。

【0024】以上のことから、本発明に使用する水可溶性樹脂としては、分子中にカルボキシル基、スルホン酸基などの少なくとも1種の親水性基を、酸価が110～

中和率 (%) = { (添加したアルカリ性化合物の当量)

／ (樹脂の酸当量) } × 100 (I)

(式中、樹脂の酸当量は中和により水可溶性樹脂となる樹脂の酸価から求められる) に基づいて算出した中和率が80～150%、なかんづく90～120%となるような量であるのが好ましい。

【0028】また、前記アルカリ性化合物による水可溶性樹脂の中和は、水および（または）有機溶剤中で中和により分散剤となる樹脂を中和し、溶解させる際に、より一層溶解が助長される点から、50℃以上、なかんづく70～90℃の温度に加熱して行なうのが好ましい。

【0029】前記水可溶性樹脂の使用量にはとくに限定はないが、第1工程の分散液中における顔料の分散性を充分に向上させるには、前記顔料100部に対して5部以上、なかんづく10部以上であるのが好ましく、また第2工程でさらに自己乳化型樹脂を添加することを考えると、分散液の粘度が上昇しすぎないように、かつ、分散

300、さらには115～300、なかんづく150～250となるように有し、スチレン単位および（または）メチルスチレン単位を50%以上、なかんづく55～70%含有する重量平均分子量が2000～20000、なかんづく2500～15000のものが好ましい。

【0025】前記水可溶性樹脂の具体例としては、たとえばスチレンーアクリル酸共重合体、スチレンーメチルスチレンーアクリル酸共重合体、スチレンーアクリル酸ーアクリル酸エステル（なお、前記エステルとは、炭素数1～4程度の低級アルキルエステルをいう、以下同様）共重合体、スチレンーメタクリル酸共重合体、スチレンーメタクリル酸ーアクリル酸エステル共重合体など；たとえばスチレンーマレイン酸共重合体、スチレンーメチルスチレンーマレイン酸共重合体、スチレンーアクリル酸エステルーマレイン酸共重合体、スチレンーメタクリル酸エステルーマレイン酸共重合体など；たとえばスチレンーアクリル酸エステルースチレンスルホン酸共重合体、スチレンーメタクリルスルホン酸共重合体、スチレンーアクリル酸エステルーアリルスルホン酸共重合体などを、ナトリウム塩、カリウム塩、アンモニウム塩などにしたものなどがあげられる。これらは単独で用いてもよく、2種以上を組み合わせ用いてもよい。

【0026】前記アルカリ性化合物にはとくに限定がないが、たとえばアンモニア；モノエタノールアミン、モルホリンなどの有機アミン類；水酸化ナトリウム、水酸化カリウム、水酸化リチウムなどのアルカリ金属塩などが有用である。これらは単独で用いてもよく、2種以上を組み合わせ用いてもよい。

【0027】前記アルカリ性化合物の添加量は、前記水可溶性樹脂中に含まれるカルボキシル基やスルホン酸基などが中和されることができる量であるのが好ましいという点から、式 (I)：

剤が過剰に入りすぎて品質がわるくならないようにするためには、100部以下、なかんづく50部以下であるのが好ましい。

【0030】前記第1工程の分散液に用いられる水媒体にはとくに限定がなく、たとえばイオン交換水、蒸留水、精製水などがあげられる。また、分散液の水の量は、たとえば前記顔料、界面活性剤および（または）水可溶性樹脂（以下、分散剤ともいう）の残量でよく、通常分散液の固形分（顔料、分散剤）濃度が4～90%程度、なかんづく10～40%となるような量でよい。

【0031】第1工程では、必要であればその他の添加剤を本発明の効果を損わない範囲で加えてもよい。

【0032】前記添加剤としては、最終的に得られる水性顔料分散体の各種物性の向上などを目的として用いられる、たとえば防腐剤、防カビ剤、消泡剤、紫外線吸収

剤、安定剤などの添加剤や、後述する水溶性溶剤の一部、糖類などがあげられる。

【0033】第1工程では、顔料を、界面活性剤および（または）水可溶性樹脂を用いて予め水媒体に分散せしめることができればよく、従来どおりの方法で分散液を調製すればよい。たとえば顔料、界面活性剤および（または）水可溶性樹脂、水媒体および必要であればその他の添加剤を混合し、湿式粉碎装置などの粉碎装置を滞留時間が3～150分となるように作動させることにより行なわれる。ここで、滞留時間とは、液が粉碎装置の中にどのくらい留まっていたかを表わす尺度をいう。

【0034】つぎに、第2工程として、第1工程で得られた分散液と自己乳化型樹脂および必要であれば架橋剤を水溶性溶剤に溶解させた液とを混合し、顔料表面に自己乳化型樹脂が固着せしめられる。

【0035】前記自己乳化型樹脂は、水媒体中に乳化剤なしで自己分散するが、これを一度、水溶性溶剤に溶解させる。この溶液を第1工程で得られた分散液と混合したとき、自己乳化型樹脂は顔料表面に吸着しながら析出すると同時に、第1工程で使用した界面活性剤および（または）水可溶性樹脂は水溶性溶剤の混入により、顔料表面から放出されると考えられる。

【0036】このようにして形成される水性顔料分散体の顔料と自己乳化型樹脂との結合は、一般の吸着による結合とは比べものにならないくらい強いので、耐溶剤性は著しく向上すると考えられる。また、自己乳化型樹脂自体が、水可溶性樹脂に比べて水に対する親和性が小さいため、耐水性の向上も期待される。

【0037】前記自己乳化型樹脂にはとくに限定はないが、たとえばアルカリ性化合物で中和した場合に自己分散性を呈する、酸価が20～110、なかんづく20～80の樹脂が好ましく用いられる。したがって、かかる酸価となるような量の、たとえばカルボキシル基、スルホン酸基などの少なくとも1種の親水性基、とくにカルボキシル基を分子中に有する重合体などが好ましい。前記自己乳化型樹脂の酸価が20より低いと、第2工程で分散液と混合させたとき顔料粒子径が大きくなったり、水性顔料分散体の保存安定性が損われやすくなる傾向が生じ、また110をこえると、水に対する溶解度が大きくなり、耐水性および耐溶剤性が期待できにくくなる傾向が生じる。

【0038】前記自己乳化型樹脂の重量平均分子量は、3000～100000、なかんづく5000～50000であるのが好ましく、3000よりも低いと水性顔料分散体の耐水性および耐溶剤性の向上が期待できず、また100000をこえると第2工程で混合させたとき、顔料粒子が大きくなりやすくなる。

【0039】前記自己乳化型樹脂の具体例としては、たとえば熱可塑性、熱硬化性あるいは変性のアクリル樹脂、ポリアクリルアミドなどのアクリル酸系樹脂；たと

えば、ポリビニルアルコール、ポリ酢酸ビニル、塩化ビニル系樹脂、ポリビニルブチラールなどのポリビニル系樹脂；ウレタン系樹脂、ポリエーテル系樹脂、エポキシ系樹脂、フッ素系樹脂、シリコン系樹脂など、あるいはこれらの混合物があげられる。これらのうちではウレタン系樹脂、アクリル系樹脂が造膜性および膜の強度と人体に対する安全性の点から好ましい。

【0040】前記自己乳化型樹脂の形態にはとくに限定がなく、たとえば粉体、水および（または）水溶性溶剤中に分散させたもの、あるいは溶解させた液状物などのいずれであってもよい。なお、水や水溶性溶剤を含む場合には、含まれる水や水溶性溶剤の量にあわせて前記水媒体の量を調整すればよい。

【0041】前記自己乳化型樹脂の正味（固形分）の使用量にはとくに限定はないが、耐水性および耐溶剤性を十分に向上させるためには、前記顔料100部に対して5部以上、なかんづく10部以上であるのが好ましく、また自己乳化型樹脂を大量に混合して、顔料粒子径を大きくしたり、粘度が上昇しすぎないように、100部以下、なかんづく60部以下であるのが好ましい。

【0042】なお、顔料表面に、自己乳化型樹脂が固着後は、この樹脂が分散剤として働くので、自己乳化型樹脂を水溶性溶剤中で中和させてから混合する必要がある。

【0043】前記自己乳化型樹脂の中和剤にはとくに限定はないが、たとえばアンモニア；モノエタノールアミン、ジエタノールアミン、トリエタノールアミン、モルホリンなどの有機アミン類；水酸化ナトリウム、水酸化カリウム、水酸化リチウムなどのアルカリ金属水酸化物などが一般的である。これらは単独で用いてもよく、2種以上を組み合わせ用いてもよい。

【0044】前記中和剤の添加量は、前記自己乳化型樹脂中に含まれるカルボキシル基やスルホン酸基などが中和されることができる量であるのが好ましいという点から、式（I）に基づいて算出した中和率が80～150%、なかんづく90～120%になるような量であるのが好ましい。

【0045】前記架橋剤は、耐水性および耐溶剤性をさらに向上させるために用いられるものであり、自己乳化型樹脂の種類に応じて適宜適したものを選択すればよい。たとえば自己乳化型樹脂がカルボキシル基を含有している場合には、エポキシ樹脂やポリアジリジン化合物が、水酸基を含有している場合には、メラミン樹脂や尿素樹脂、イソシアネート基を有する樹脂などがあげられる。

【0046】前記架橋剤の使用量も自己乳化型樹脂の種類に応じて適宜適した量を使用すればよいが、一般的には正味の自己乳化型樹脂100部に対して3～35部、なかんづく5～18部である。

【0047】前記水溶性溶剤は、20℃で、水と自由に

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混合できる水溶性溶剤であり、前記自己乳化型樹脂を溶解させるものであればその種類にとくに制限はないが、たとえばアセトン；アルコール類のメタノール、エタノール、*n*-プロパノール、イソプロパノールなど；グリコール類のエチレングリコール、プロピレングリコール、ジエチレングリコール、ジプロピレングリコール、テトラエチレングリコールなど；グリセリン；多価アルコールのエーテル類のジエチレングリコールジエチルエーテル、ジエチレングリコールモノブチルエーテル、エチレングリコールモノエチルエーテル、エチレングリコールモノブチルエーテル、メチルカルビトール、エチルカルビトール、ブチルカルビトール、トリエチレングリコールモノメチルエーテル、トリエチレングリコールモノエチルエーテル、プロピレングリコールモノメチルエーテルなど；含窒素化合物類のトリエタノールアミンなど；ジメチルスルホキシドなどの20℃で水と自由に混合できるものがあげられる。これらは単独で用いてもよく、2種以上を組み合わせ用いてもよい。これらのうちでは自己乳化型樹脂をよく溶かし、水より沸点が低く、第1工程の分散液との混合で拡散がスムーズに行なわれる点から、アセトン、エタノールなどが好ましい。

【0048】前記水溶性溶剤の使用量にはとくに制限はないが、前記自己乳化型樹脂を溶解させたとき、その粘度があまり高くないようにするためには、正味の自己乳化型樹脂100部に対して100部以上、なかんづく150部以上であることが好ましく、また過剰に入りすぎて品質がわるくならないようにするためには、15000部以下、なかんづく10000部以下であるのが好ましい。

【0049】第2工程では、顔料表面に自己乳化型樹脂を固着せしめることができればよく、とくに限定はないが、たとえば第1工程で得られた分散液と自己乳化型樹脂および必要であれば架橋剤を水溶性溶剤に溶解させた液とを混合し、30～60分間攪拌することにより行なわれる。

【0050】第1工程で得られた分散液と自己乳化型樹脂などを溶解させた溶液とを混合させる際の混合のさせ方としては、前記分散液の固形分濃度および粘度、前記溶液の自己乳化型樹脂濃度および粘度、水溶性溶剤の種類などにより異なるが、前記分散液または前記溶液が十分に、またすばやく拡散できるように、攪拌を充分に行ないながら、どちらかを滴下させることが好ましい。また、混合する場合の前記分散液と前記溶液の容積比は98/2～66/34であるのが水性顔料分散体の安定性の点から好ましい。さらに、混合させる場合の温度としては、水溶性溶剤の沸点より20℃程度低い温度で室温以上であるのが好ましい。

【0051】前記溶液中に、架橋剤を添加している場合は、両液を混合したのち、適切な条件で、加熱攪拌するなどして架橋反応を進めてもよい。また、用途によって

は、水性顔料分散体中の水溶性溶剤を蒸留により除去することもできる。

【0052】このようにして自己乳化型樹脂を顔料表面に固着させることにより、製造される水性顔料分散体は、優れた耐水性、耐溶剤性を発揮するものとなる。

【0053】

【実施例】以下、実施例に基づいて本発明の製造方法の有効性をさらに詳細に示すが、もちろん本発明はこれらに限定されるものではない。

【0054】なお、以下の実施例および比較例で用いた評価方法を、以下にまとめて示す。

【0055】（平均粒子径の測定）所定の分散液または水性顔料分散体を、顔料濃度が0.1g/lとなるようにイオン交換水で希釈し、該希釈液を用いてリーズ・アンド・ノースラップ社製のマイクロトラックUPAにて分散粒子の平均粒子径を測定する。

【0056】（耐水性）所定の分散液または水性顔料分散体を、OHPシートに1.5ミルのアプリケーションにて展色し、125℃で10分間乾燥させたのち、3分間水に浸漬し、色のにじみの有無を目視で判定して以下の基準で評価する。

○：色のにじみがなく良好なもの

△：軽度の異常（色のにじみ）が認められたもの

×：好ましくない異常（色のにじみ）が認められたもの

【0057】（耐溶剤性）所定の分散液または水性顔料分散体を、OHPシートに1.5ミルのアプリケーションにて展色し、125℃で10分間乾燥させたのち、3分間溶剤（エタノール/水（重量比）：1/1）に浸漬し、色のにじみの有無を目視で判定して耐水性に準じて評価する。

【0058】実施例1

黄顔料（ピグメント・イエロー83、一次粒子径：0.04μm）25部、スチレン-アクリル酸共重合体（スチレン/アクリル酸（重量比）：70/30、酸価：170、重量平均分子量：12000）5部のアンモニア中和物（中和率：110%）、グリセリン5部、防腐剤（ベストサイドー1177A（大日本インキ化学工業（株）製））（以下、防腐剤という）0.1部およびイオン交換水を加え、固形分濃度が30%となるように調整した水性顔料組成物について、湿式粉碎装置を滞留時間が15分となるように作動させて分散液を得（第1工程）、分散粒子の平均粒子径を測定した。

【0059】つぎに、系の温度を30℃に保ち、前記分散液100部を攪拌しながら、自己乳化型樹脂であるウレタン系樹脂エマルジョン（NeoRad NR-440（商品名）、ゼネカ（株）製、樹脂成分40%（水中）、酸価（中和前）：約25、重量平均分子量：7200）（以下、NeoRad NR-440という）18.8部をアセトン30部に溶解させたものを滴下し、そののち30℃で40分間攪拌して水性顔料分散体を得（第2工程）、分散粒子

の平均粒子径を測定し、さらに耐水性および耐溶剤性を評価した。

【0060】結果を表1に示す。

【0061】比較例1

実施例1の第1工程で得られた分散液を用い、耐水性および耐溶剤性を前記方法により評価した。

【0062】結果を表1に示す。

【0063】実施例2

赤顔料（ピグメント・レッド22、一次粒子径：0.06 μm ）25部、スチレン- α -メチルスチレン-アクリル酸共重合体（スチレン/ α -メチルスチレン/アクリル酸（重量比）：30/25/45、酸価：234、重量平均分子量：9000）6.3部のアンモニア中和物（中和率：105%）、グリセリン5部、防腐剤0.1部およびイオン交換水を加え、固形分濃度が30%となるように調整した水性顔料組成物について、湿式粉碎装置を滞留時間が15分となるように作動させて分散液を得（第1工程）、分散粒子の平均粒子径を測定した。

【0064】つぎに、系の温度を30℃に保ち、前記分散液100部を攪拌しながら、NeoRad NR-440 20部をアセトン30部に溶解させたものを滴下し、そののち30℃で40分間攪拌して水性顔料分散体を得（第2工程）、分散粒子の平均粒子径を測定し、さらに耐水性および耐溶剤性を評価した。

【0065】結果を表1に示す。

【0066】比較例2

実施例2の第2工程で使用した水溶性溶剤のアセトンをベンゼンに変更し、第2工程終了後分液ロートでベンゼンを除去するほかは、実施例2と同様にして水性顔料分散体を得、分散粒子の平均粒子径を測定し、さらに耐水性および耐溶剤性を評価した。

【0067】結果を表1に示す。

【0068】実施例3

青顔料（ピグメント・ブルー15：6、一次粒子径：0.06 μm ）24部、スチレン-マレイン酸共重合体（スチレン/マレイン酸（重量比）：60/40、酸価：190、重量平均分子量：3000）8.5部のアンモニア中和物（中和率：107%）、グリセリン5部、防腐剤0.1部およびイオン交換水を加え、固形分濃度が30%となるように調整した水性顔料組成物について、湿式粉碎装置を滞留時間が15分となるように作動させて分散液を得（第1工程）、分散粒子の平均粒子径を測定した。

【0069】つぎに、系の温度を30℃に保ち、前記分散液100部を攪拌しながら、NeoRad NR-440 19部をアセトン30部に溶解させたものを滴下し、そののち30℃で40分間攪拌して水性顔料分散体を得（第2工程）、分散粒子の平均粒子径を測定し、さらに耐水性および耐溶剤性を評価した。

【0070】結果を表1に示す。

【0071】比較例3

実施例3の第2工程で使用した自己乳化型樹脂をNeoRad NR-440からNeoRez R-960（商品名）（ゼネカ（株）製、酸価：約20、重量平均分子量：300000~700000）に変更したほかは、実施例3と同様にして水性顔料分散体を得、分散粒子の平均粒子径を測定し、さらに耐水性および耐溶剤性を評価した。

【0072】結果を表1に示す。

【0073】実施例4

緑顔料（ピグメント・グリーン7、一次粒子径：0.05 μm ）25部、スチレン-メタクリル酸共重合体（スチレン/メタクリル酸（重量比）：65/35、酸価：170、重量平均分子量：8500）8.8部のアンモニア中和物（中和率：108%）、グリセリン5部、防腐剤0.1部およびイオン交換水を加え、固形分濃度が30%となるように調整した水性顔料組成物について、湿式粉碎装置を滞留時間が15分となるように作動させて分散液を得（第1工程）、分散粒子の平均粒子径を測定した。

【0074】つぎに、系の温度を30℃に保ち、前記分散液100部を攪拌しながら、NeoRad NR-440 19部をアセトン30部に溶解させたものを滴下し、そののち30℃で40分間攪拌して水性顔料分散体を得（第2工程）、分散粒子の平均粒子径を測定し、さらに耐水性および耐溶剤性を評価した。

【0075】結果を表1に示す。

【0076】比較例4

実施例4の第1工程で使用した水可溶性樹脂を、スチレン-メタクリル酸共重合体からNeoRad NR-440に変更するほかは、実施例4と同様にして第1工程を行なって分散液を得、分散粒子の平均粒子径を測定し、さらに耐水性および耐溶剤性を評価した。

【0077】結果を表1に示す。

【0078】

【表1】

表 1

	第 1 工程分散液	水性顔料分散体		
	平均粒子径 (nm)	平均粒子径	耐水性	耐溶剤性
実施例 1	132	135	○	○
比較例 1	132	—	△	×
実施例 2	113	117	○	○
比較例 2	113	210	×	×
実施例 3	125	130	○	○
比較例 3	125	200	○	△
実施例 4	117	120	○	○
比較例 4	190	—	△	△

【0079】表 1 に示された結果から、本発明の製法により得られた実施例 1～4 の水性顔料分散体は、第 1 工程の分散が容易で、かつ第 2 工程で自己乳化型樹脂を滴下しても増粒しないものであり、また耐水性および耐溶剤性に優れていることがわかる。

【0080】一方、従来の水可溶性樹脂を使用した第 1 工程だけの製造方法により得られた比較例 1 の分散液では、耐水性と耐溶剤性で劣っている。また、水に対する親和性の小さい溶剤を使用した比較例 2 と重量平均分子量の大きい自己乳化型樹脂を使用した比較例 3 では、第 2 工程で自己乳化型樹脂を滴下したとき増粒傾向がみられる。さらに、第 1 工程において、水可溶性樹脂のかわりに自己乳化型樹脂を用いて顔料を分散させた比較例 4

では、微粒子化が困難であることがわかる。

【0081】

【発明の効果】本発明の製法によれば、従来の方法に 1 つの工程を加えるだけで、微粒子で保存安定性、耐水性、耐溶剤性に優れた水性顔料分散体を短時間で容易に製造することができる。

【0082】また、本発明の製法により得られる水性顔料分散体は、前記のごとき特性を有するものであるため、水性塗料、印刷インキ、筆記用インキ、捺染だけでなく、たとえばカラーフィルター、インクジェット用インキなどの色相、着色力、透明性の点で高い物性が要求される分野においても好適に用いることができる。

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CLAIMS

[Claim(s)]

[Claim 1] (1) the manufacture approach of the watercolor pigment dispersing element which consists of the 2nd process which the dispersion liquid obtained at the 1st process which makes a water medium distribute a pigment beforehand using a surfactant and (or) water-soluble resin, and (2) the 1st process, and the liquid made to dissolve the self-emulsification mold resin which has weight average molecular weight in the range of 3000-100000 in a water soluble solvent are mixed [process], and makes a pigment front face fix self-emulsification mold resin.

[Claim 2] (1) the manufacture approach of a watercolor pigment dispersing element that the dispersion liquid obtained at the 1st process which makes a water medium distribute a pigment beforehand using a surfactant and (or) water-soluble resin, and (2) the 1st process, and weight average molecular weight consist of the 2nd process which the liquid made to dissolve the self-emulsification mold resin and the cross linking agent in the range of 3000-100000 in a water soluble solvent is mixed [process], and makes a pigment front face fix self-emulsification mold resin and a cross linking agent.

[Claim 3] the manufacture approach according to claim 1 or 2 that said surfactants are a nonionic surfactant and (or) an anionic detergent.

[Claim 4] the manufacture approach according to claim 1 or 2 that the weight average molecular weight in which said water-soluble resin has at least one sort of hydrophilic radicals of a carboxyl group and a sulfonic group in a molecule, and contains a styrene unit and (or) a methyl styrene unit 50% of the weight or more is the polymer of 2000-20000.

[Claim 5] The manufacture approach according to claim 1 or 2 that said self-emulsification mold resin is urethane system resin or acrylic resin.

[Claim 6] The manufacture approach according to claim 1, 2, or 5 which has the acid number of said self-emulsification mold resin in the range of 20-110.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of a watercolor pigment dispersing element useful to a water paint, water color ink, textile printing or a color filter, the toner for ink jets, etc.

[0002]

[Description of the Prior Art] From the former, the pigment dispersing element has been broadly used for applications, such as a coating, printing ink, writing-materials ink, and textile printing. And an application is being expanded to the object for ink jets, or color filters, therefore recent years require the improvement in the engine performance of a pigment dispersing element.

[0003] Generally a water pigment dispersing element is stabilized by a non-ion-operation or ion-operation.

[0004] A hydrophobic part adsorbs with a pigment, a hydrophilic part extends underwater, and the nonionic surfactant or water soluble resin stabilized according to a non-ion-operation prevents the re-condensation between pigment particles entropy-wise or in three dimensions.

[0005] Moreover, in the case of the cationic surfactant stabilized according to an ion-operation, an anionic detergent, or neutralization mold resin, by ionizing first, the part in which a hydrophilic property appears extends underwater, and an electric double layer is formed in the perimeter of a pigment particle. And this electric double layer induces electric repulsive force, and prevents the re-condensation between pigment particles.

[0006] As for the watercolor pigment dispersing element currently distributed by such stabilization device, various problems appear by the application. For example, the coating which used the pigment dispersing element distributed using the surfactant has the problem that the water resisting property of the paint film obtained is bad. Moreover, since the pigment and the dispersant are paying well only by weak coupling called adsorption, a general pigment dispersing element has the problem that solvent resistance is weak, weakly that is, in the polar change in a water medium.

[0007] This invention is made in view of said conventional technique, and aims at offering the manufacture approach of a watercolor pigment dispersing element of having excelled in preservation stability, a water resisting property, and solvent resistance by the particle.

[0008]

[Means for Solving the Problem] this invention persons came to complete this invention, as a result of repeating examination wholeheartedly in order to obtain the watercolor pigment dispersing element which was excellent in preservation stability, a water resisting property, and solvent resistance with the particle.

[0009] that is, this invention makes a water medium distribute (1) pigment beforehand using a surfactant and (or) water-soluble resin — the 1st process (2) The dispersion liquid obtained at the 1st process and the liquid made to dissolve the self-emulsification mold resin which has weight average molecular weight in the range of 3000-100000 in a water soluble solvent are mixed. The manufacture approach of the watercolor pigment dispersing element which consists of the 2nd process which makes a pigment front face fix self-emulsification mold resin (claim 1), (1) — a water medium is made to distribute a pigment beforehand using a surfactant and (or) water-soluble resin —

the 1st process (2) The liquid made to dissolve the self-emulsification mold resin and the cross linking agent which have the dispersion liquid obtained at the 1st process and weight average molecular weight in the range of 3000-100000 in a water soluble solvent is mixed. The manufacture approach of the watercolor pigment dispersing element which consists of the 2nd process which makes a pigment front face fix self-emulsification mold resin and a cross linking agent (claim 2), the manufacture approach (claim 3) according to claim 1 or 2 that said surfactants are a nonionic surfactant and (or) an anionic detergent — Said water-soluble resin has at least one sort of hydrophilic radicals of a carboxyl group and a sulfonic group in a molecule, a styrene unit and (or) a methyl styrene unit 50% of the weight The manufacture approach according to claim 1 or 2 that the weight average molecular weight contained above is the polymer of 2000-20000 (claim 4), (It is hereafter called %) It is related with the manufacture approach (claim 5) according to claim 1 or 2 that said self-emulsification mold resin is urethane system resin or acrylic resin, and the manufacture approach (claim 6) according to claim 1, 2, or 5 which has the acid number of said self-emulsification mold resin in the range of 20-110.

[0010]

[Embodiment of the Invention] a pigment is made to distribute beforehand first in this invention, using a surfactant and (or) water-soluble resin as the 1st process by the water medium At this time, as long as it is required, other additives may also be added beforehand.

[0011] There is especially no limitation in said pigment, for example, various inorganic pigments, such as oxide; cadmium yellow, such as various organic pigments, such as polycyclic type pigment; color chelates, such as azo pigment; phthalocyanine pigments, such as an azo lake, insoluble azo pigment, a disazo condensation pigment, and a chelate azo pigment, a perylene pigment, a thioindigo pigment, an isoindolinone pigment, and a kino FUTARON pigment, and titanium oxide, red ocher, chromic oxide, iron black, Chrome Vermilion, Berlin blue, ultramarine blue, and Synthetic Ochre, carbon black, etc. are raised. These may be used independently and may be used combining two or more sorts.

[0012] As an example of said organic pigment, for example The PIKUMENTO yellow 1 (C. I.11680), The pigment yellow 3 (C. I.11710), the pigment yellow 74 (C. I.11741), The pigment yellow 83 (C. I.21108), the pigment yellow 106, the pigment yellow 108 (C. I.68240), The pigment yellow 117, the pigment yellow 126, the pigment yellow 139, the pigment yellow 185, pigment Orange 5 (C. I.12075), Pigment Orange 67, the pigment red 3 (C. I.12120), The pigment red 22 (C. I.12315), the pigment red 48:1 (C. I.15865:1), The pigment red 48:4 (C. I.15865:4), the pigment red 101 (C. I.77491), The pigment red 112 (C. I.12370), the pigment red 123 (C. I.71145), The pigment red 169 (C. I.45160:2), the pigment violet 23 (C. I.51319), The pigment violet 27 (C. I.42555:3), the pigment blue 1 (C. I.42595:3), The pigment blue 15:1 (C. I.74160), the pigment blue 15:3 (C. I.74160), The pigment blue 15:6 (C. I.74160), the pigment blue 61 (C. I.42765:1), pigment Green 7 (C. I.74260), pigment Green 36 (C. I.74265), etc. are raised.

[0013] Moreover, the pigment yellow 42 (C. I.77492), pigment White 6 (C. I.77981), the pigment blue 27 (C. I.77510), the pigment blue 29 (C. I.77007), the pigment black 7 (C. I.77266), etc. are raised as an example of said inorganic pigment.

[0014] In addition, you may be any, such as what there is no limitation especially in the gestalt of said pigment, and performed various surface treatment, fine particles, and an aqueous paste. These may be used independently and may be used combining or more 2 kind. Among these, the point that dispersibility is good to an aqueous paste is desirable.

[0015] Moreover, when dispersibility is taken into consideration, as for the primary particle diameter of said pigment, it is desirable that they are usually about 0.1 micrometers or less and 0.01-0.06 micrometers of *****.

[0016] It is desirable to adjust so that it may become 80% or less and 40% or less of *****, since it becomes the cause by which a diffusion rate becomes slow in case it will mix with a water soluble solvent at the 2nd process, if it is desirable to adjust so that the concentration in the dispersion liquid obtained at the 1st process in order to obtain sufficient tinting strength, although there is especially no limitation in the loadings of said pigment may become 1% or more and 3% or more of ***** and the viscosity of dispersion liquid is too high, and particle diameter becomes large.

[0017] as long as it has been used from the former as said surfactant and (or) water-soluble resin,

there is especially no limitation. For example, water-soluble resin, such as surfactants, such as a cationic surfactant, an anionic detergent, and a nonionic surfactant, and water-soluble acrylic resin, water-soluble nylon system resin, water-soluble epoxy system resin, water-soluble naturally-occurring polymers, is raised. these — independent — business — you may use with a sufficient potato combining two or more sorts. That is, since distribution of the 1st process is the same as the process of the conventional watercolor pigment dispersing element, it has the merit which the conventional manufacturing facility can use as it is.

[0018] As a nonionic surfactant of said surface active agents, the nonionic surfactant of polyoxyethylene alkyl ether, polyoxyethylene alkyl aryl ether, a polyoxyethylene oxypropylene block copolymer, a sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, polyoxyethylene sorbitol fatty acid ester, a glycerine fatty acid ester, polyoxyethylene fatty acid ester, polyoxyethylene alkylamine, and a fluorine system, the nonionic surfactant of a silicone system, etc. are raised. These may be used independently and may be used combining or more 2 kind.

[0019] As an anionic detergent of said surfactants, a fatty-acid salt, an alkyl-sulfuric-acid ester salt, alkylaryl sulfonates, alkyl naphthalenesulfonate, a dialkyl sulfonate, dialkyl sulfo succinate, alkyl diaryl ether disulfon acid chloride, alkyl phosphate, a polyoxyethylene-alkyl-ether sulfate, a polyoxyethylene-alkyl-aryl-ether sulfate, a naphthalene sulfonic-acid formalin condensate, polyoxyethylene alkyl phosphate, a glycerol borate fatty-acid-ester salt, etc. are raised. These may be used independently and may be used combining or more 2 kind.

[0020] As a cationic surfactant of said surfactants, alkylamine salt, quarternary ammonium salt, sulfonium salt, phosphonium salt, etc. are raised. These may be used independently and may be used combining two or more sorts.

[0021] Although there is no limitation especially in the amount of said surfactant used, in order to fully raise the dispersibility of the pigment in the dispersion liquid of the 1st process If it is desirable that they are the 5 or more sections and the 10 or more section of ***** and it considers adding self-emulsification mold resin further at the 2nd process to said pigment 100 weight section (henceforth the section), so that the viscosity of dispersion liquid may not go up too much And in order for a surfactant to enter too much superfluously and to make it quality not worsen, it is desirable that they are the 100 or less sections and the 50 or less section of *****.

[0022] Said water-soluble resin is what is used in order to distribute a pigment. Although there is especially no limitation in the class, improve the balance of the hydrophobic group which sticks to a pigment, and the hydrophilic group developed in a water medium, and the dispersion effect of water-soluble resin is heightened. hydrophobic monomeric units, such as for example, a styrene unit from the point of raising dispersibility, and a methyl styrene unit, — water-soluble resin of 55 – 70% of ***** is preferably desirable 50% or more and further 50 to 70% in a styrene unit and (or) a methyl styrene unit. Moreover, when improvement in dispersibility is taken into consideration, as for the weight average molecular weight of this water-soluble resin, it is desirable that they are 2000–20000, and ***** 2500–15000.

[0023] That to which the acid number which neutralizes with an alkaline compound and presents water solubility as said water-soluble resin neutralized the resin of 115–300, and ***** 150–250 with the alkaline compound to 110–300, and a pan is desirable. Therefore, the polymer which has in a molecule at least one sort of hydrophilic radicals, such as an amount which serves as this acid number, for example, a carboxyl group, and a sulfonic group, is desirable.

[0024] as the water-soluble resin used for this invention from the above thing — the inside of a molecule — at least one sort of hydrophilic radicals, such as a carboxyl group and a sulfonic group, — the acid number — 110–300 — further — the thing of 2000–20000, and ***** 2500–15000 has the desirable weight average molecular weight which has so that it may become 115–300, and ***** 150–250, and contains a styrene unit and (or) a methyl styrene unit 55 – 70% of ***** 50% or more.

[0025] As an example of said water-soluble resin, for example A styrene-acrylic-acid copolymer, A styrene-methyl styrene-acrylic-acid copolymer, styrene-acrylic-acid-acrylic ester (in addition with said ester) Like the following which says with a carbon number of about one to four low-grade alkyl ester, a copolymer, ;, for example, styrene-maleic-acid copolymers, such as a styrene-methacrylic-acid copolymer and a styrene-methacrylic-acid-acrylic ester copolymer, A styrene-methyl styrene-

maleic-acid copolymer, a styrene-acrylic ester-maleic-acid copolymer, ;, for example, styrene-acrylic ester-styrene sulfonic-acid copolymers, such as a styrene-methacrylic ester-maleic-acid copolymer, What used the styrene-methacrylic sulfonic-acid copolymer, the styrene-acrylic ester-allyl compound sulfonic-acid copolymer, etc. as sodium salt, potassium salt, ammonium salt, etc. is raised. These may be used independently and may be used combining two or more sorts.

[0026] Although there is no limitation especially in said alkaline compound, alkali-metal salts, such as organic amines; sodium hydroxides, such as ammonia; monoethanolamine and a morpholine, a potassium hydroxide, and a lithium hydroxide, etc. are useful, for example. These may be used independently and may be used combining two or more sorts.

[0027] formula (I) from the point that it is desirable that it is the amount by which the carboxyl group contained in said water-soluble resin, a sulfonic group, etc. can be neutralized as for the addition of said alkaline compound: neutralization-index (%) = $\frac{\text{[(equivalent of the added alkaline compound)]}}{\text{[acid equivalent of resin]}} \times 100$ (I)

It is desirable that it is the amount from which it is based [(the acid equivalent of resin is calculated among a formula from the acid number of the resin which turns into water-soluble resin by neutralization), and], and the computed neutralization index serves as 90 - 120% of ***** 80 to 150%.

[0028] moreover, in case neutralization of water-soluble resin with said alkaline compound neutralizes the resin which serves as a dispersant by neutralization and makes it dissolve in water and (or) an organic solvent, it is desirable to carry out from the point that the dissolution is promoted further, by heating to 50 degrees C or more and the temperature of 70-90 degree C of *****.

[0029] Although there is especially no limitation in the amount of said water-soluble resin used, in order to fully raise the dispersibility of the pigment in the dispersion liquid of the 1st process If it is desirable that they are the 5 or more sections and the 10 or more section of ***** and it considers adding self-emulsification mold resin further at the 2nd process to said pigment 100 section, so that the viscosity of dispersion liquid may not rise too much And in order for a dispersant to enter too much superfluously and to make it quality not worsen, it is desirable that they are the 100 or less sections and the 50 or less section of *****.

[0030] There is no limitation especially in the water medium used for the dispersion liquid of said 1st process, for example, ion exchange water, distilled water, purified water, etc. are raised. moreover, the amount of the water of dispersion liquid — for example, it is good at the residue of said pigment, a surfactant, and (or) water-soluble resin (henceforth a dispersant), and good in an amount from which the solid content (pigment, dispersant) concentration of dispersion liquid usually serves as 10 - 40% of ***** about 4 to 90%.

[0031] At the 1st process, as long as it is required, other additives may be added in the range which does not spoil the effectiveness of this invention.

[0032] As said additive, for the purpose of improvement in the various physical properties of the watercolor pigment dispersing element finally obtained etc., it is used, for example, additives, such as antiseptics, an antifungal agent, a defoaming agent, an ultraviolet ray absorbent, and a stabilizer, a part of water soluble solvent mentioned later, a saccharide, etc. are raised.

[0033] what is necessary is just to prepare dispersion liquid by the approach as usual at the 1st process that what is necessary is just to be able to make a water medium distribute a pigment beforehand using a surfactant and (or) water-soluble resin for example, if required, other additives will be mixed, and it is carried out a pigment, a surfactant and (or) water-soluble resin, a water medium, and by operating grinding equipments, such as wet-grinding equipment, so that the residence time may become 3 - 150 minutes. Here, the residence time means the scale showing how much liquid had stopped into grinding equipment.

[0034] Next, if required, the dispersion liquid obtained at the 1st process, self-emulsification mold resin, and the liquid made to dissolve a cross linking agent in a water soluble solvent will be mixed, and self-emulsification mold resin will be made to fix as the 2nd process by the pigment front face.

[0035] Although said self-emulsification mold resin carries out self-distribution without an emulsifier into a water medium, it dissolves this in a water soluble solvent once. it is thought that the surfactant and (or) water-soluble resin which were used at the 1st process are emitted by mixing of a water soluble solvent from a pigment front face while it deposits sticking to self-emulsification mold resin

on a pigment front face, when this solution is mixed with the dispersion liquid obtained at the 1st process.

[0036] Thus, since it is as strong as association with the pigment of a watercolor pigment dispersing element and self-emulsification mold resin which are formed does not become a thing compared with association by general adsorption, it is thought that solvent resistance improves remarkably. Moreover, since compatibility [as opposed to water in self-emulsification mold resin itself] is small compared with water-soluble resin, waterproof improvement is also expected.

[0037] Although there is especially no limitation in said self-emulsification mold resin, when an alkaline compound neutralizes, for example, the resin of 20-110, and ***** 20-80 is preferably used for the acid number which presents self-dispersibility. Therefore, the polymer which has in a molecule at least one sort of hydrophilic radicals, such as an amount which serves as this acid number, for example, a carboxyl group, and a sulfonic group, especially a carboxyl group is desirable. If pigment particle diameter becomes large, the inclination for the preservation stability of a watercolor pigment dispersing element to disadvantage-crack-come to be easy arises and 110 is surpassed when the acid number of said self-emulsification mold resin was lower than 20 and it is made to mix with dispersion liquid at the 2nd process, the solubility to water will become large and the inclination it to become impossible that it is hard to expect a water resisting property and solvent resistance will arise.

[0038] If it is desirable that they are 3000-100000, and ***** 5000-50000 as for the weight average molecular weight of said self-emulsification mold resin and it is lower than 3000, improvement in the water resisting property of a watercolor pigment dispersing element and solvent resistance is not expectable, and when 100000 was surpassed and it is made to mix at the 2nd process, a pigment particle becomes easy to become large.

[0039] As an example of said self-emulsification mold resin, such mixture, such as polyvinyl system resin; urethane system resin, such as acrylic-acid system resin [, such as acrylic resin of thermoplasticity, thermosetting, or denaturation and polyacrylamide,],, for example, polyvinyl alcohol, polyvinyl acetate, vinyl chloride system resin, and a polyvinyl butyral, polyether system resin, epoxy system resin, fluorine system resin, and silicone system resin, is raised, for example. Among these, urethane system resin and acrylic resin are desirable from the point of film formation nature and the safety to membranous reinforcement and the membranous body.

[0040] you may be any, such as a thing which there is no limitation especially in the gestalt of said self-emulsification mold resin, for example, was distributed in fine particles, water, and (or) a water soluble solvent, or a liquefied object in which it was made to dissolve. In addition, what is necessary is just to adjust the amount of said water medium in accordance with the amount of the water contained or a water soluble solvent, when water and a water soluble solvent are included.

[0041] In order to fully raise a water resisting property and solvent resistance, although there is especially no limitation in the amount of the net (solid content) used of said self-emulsification mold resin, it is desirable [it is desirable that they are the 5 or more sections and the 10 or more section of ***** to said pigment 100 section, and] that they are the 100 or less sections and the 60 or less section of ***** so that self-emulsification mold resin is mixed in large quantities, pigment particle diameter may not be enlarged or viscosity may not rise too much.

[0042] In addition, since this resin works on a pigment front face as a dispersant after self-emulsification mold resin's fixing, after making it neutralize self-emulsification mold resin in a water soluble solvent, it is necessary to mix.

[0043] Although there is especially no limitation in the neutralizer of said self-emulsification mold resin, alkali-metal hydroxides, such as organic amines; sodium hydroxides, such as ammonia; monoethanolamine, diethanolamine, triethanolamine, and a morpholine, a potassium hydroxide, and a lithium hydroxide, etc. are common, for example. These may be used independently and may be used combining two or more sorts.

[0044] As for the addition of said neutralizer, it is desirable that it is the amount to which the neutralization index computed based on the formula (I) becomes 90 - 120% of ***** from the point that it is desirable that it is the amount by which the carboxyl group contained in said self-emulsification mold resin, a sulfonic group, etc. can be neutralized, 80 to 150%.

[0045] Said cross linking agent is used in order to raise a water resisting property and solvent

resistance further, and it should just choose what was suitable suitably according to the class of self-emulsification mold resin. For example, when self-emulsification mold resin contains the carboxyl group and the epoxy resin and the poly aziridine compound contain the hydroxyl group, melamine resin, a urea-resin, the resin that has an isocyanate radical are raised.

[0046] Although what is necessary is just to use the amount for which the amount of said cross linking agent used was also suitable suitably according to the class of self-emulsification mold resin, generally it is the five to 18 section above all the three to 35 section to the self-emulsification mold resin 100 net section.

[0047] Said water soluble solvent is 20 degrees C, and it is a water soluble solvent free mixable with water. Although there will be especially no limit in the class if said self-emulsification mold resin is dissolved For example, an acetone; The methanol of alcohols, ethanol, n-propanol, Isopropanol etc.; The ethylene glycol of glycols, propylene glycol, ; glycerols, such as a diethylene glycol, dipropylene glycol, and tetraethylene glycol; Diethylene-glycol diethylether of the ether of polyhydric alcohol, The diethylene-glycol monobutyl ether, ethylene glycol monoethyl ether, Ethylene glycol monobutyl ether, methyl carbitol, ethyl carbitol, Butyl carbitol, the triethylene glycol monomethyl ether, Triethanolamine of; ** nitrogen compounds, such as the triethylene glycol monoethyl ether and propylene glycol monomethyl ether, etc.; the expenses [degrees C /, such as dimethyl sulfoxide, / 20] of a thing free mixable with water are covered. These may be used independently and may be used combining two or more sorts. Among these, self-emulsification mold resin is often melted, the boiling point is lower than water, and the acetone from the point that diffusion is smoothly performed by mixing with the dispersion liquid of the 1st process, ethanol, etc. are desirable.

[0048] Although there is especially no limit in the amount of said water soluble solvent used, when dissolving said self-emulsification mold resin, in order for it to enter too much that they are the 100 or more sections and the 150 or more section of ***** preferably and superfluously and to make it quality not worsen [as opposed to / in order to make it the viscosity not become not much high / the self-emulsification mold resin 100 net section], it is desirable that they are the 15000 or less sections and the 10000 or less section of *****.

[0049] At the 2nd process, that what is necessary is just to be able to make a pigment front face fix self-emulsification mold resin, although there is especially no limitation, if required, the dispersion liquid obtained, for example at the 1st process, self-emulsification mold resin, and the liquid made to dissolve a cross linking agent in a water soluble solvent will be mixed, and it is carried out by agitating for 30 - 60 minutes.

[0050] Although mixing at the time of mixing the dispersion liquid obtained at the 1st process and the solution in which self-emulsification mold resin etc. was dissolved carries out and it changes as a direction with classes of the solid content concentration of said dispersion liquid and viscosity, the self-emulsification mold resin concentration of said solution and viscosity, and water soluble solvent etc., the thing which is fully a line about churning and which is made for either to be dropped without moving from its seat is desirable so that said dispersion liquid or said solution may diffuse quickly again enough. Moreover, as for the volume ratio of said dispersion liquid in the case of mixing, and said solution, it is desirable from the point of the stability of a watercolor pigment dispersing element that it is 98 / 2 - 66/34. Furthermore, it is desirable that it is beyond a room temperature as temperature in the case of making it mix at temperature lower about 20 degrees C than the boiling point of a water soluble solvent.

[0051] Into said solution, when the cross linking agent is added, after mixing both liquid, it is suitable conditions, and heating churning may be carried out and crosslinking reaction may be advanced. Moreover, depending on an application, the water soluble solvent in a watercolor pigment dispersing element is also removable with distillation.

[0052] Thus, by making a pigment front face fix self-emulsification mold resin, the watercolor pigment dispersing element manufactured demonstrates the outstanding water resisting property and solvent resistance.

[0053]

[Example] Hereafter, although the effectiveness of the manufacture approach of this invention is further shown in a detail based on an example, of course, this invention is not limited to these.

[0054] In addition, the evaluation approach used in the following examples and examples of a

comparison is shown collectively below.

[0055] (Measurement of mean particle diameter) Predetermined dispersion liquid or a predetermined watercolor pigment dispersing element is diluted with ion exchange water so that pigment concentration may serve as 0.1 g/l, and the mean particle diameter of a particulate material is measured using this diluent by micro truck UPA by Leeds - and - North lap company.

[0056] (Water resisting property) After carrying out drawdown of predetermined dispersion liquid or a predetermined watercolor pigment dispersing element to an OHP sheet by the 1.5-mil applicator and drying it for 10 minutes at 125 degrees C, it is immersed in water for 3 minutes, the existence of a blot of a color is judged visually, and the following criteria estimate.

O : — a blot of a color — there is nothing — good thing **: — thing x: in which slight abnormalities (blot of a color) were accepted — what the abnormalities (blot of a color) which are not desirable were accepted in [0057] (Solvent resistance) After carrying out drawdown of predetermined dispersion liquid or a predetermined watercolor pigment dispersing element to an OHP sheet by the 1.5-mil applicator and drying it for 10 minutes at 125 degrees C, it is immersed in a solvent (ethanol/water (weight ratio): 1/1) for 3 minutes, the existence of a blot of a color is judged visually, and it evaluates according to a water resisting property.

[0058] The ammonia neutralization object (neutralization index: 110%) of the example 1 yellow pigment (pigment yellow 83 diameter of primary particle: 0.04 micrometers) 25 section, and the styrene-acrylic-acid copolymer (styrene [/] acrylic acid (weight ratio): 70/30, acid-number:170, weight-average-molecular-weight:12000) 5 section, the glycerol 5 section, the antiseptics (best side - 1177A (Dainippon Ink & Chemicals, Inc. make)) (henceforth antiseptics) 0.1 section, and ion exchange water About the watercolor pigment constituent adjusted in addition so that solid content concentration might become 30%, wet-grinding equipment was operated so that the residence time might become 15 minutes, dispersion liquid were obtained (the 1st process), and the mean particle diameter of a particulate material was measured.

[0059] The urethane system resin emulsion which is self-emulsification mold resin while keeping the temperature of a system at 30 degrees C and agitating said dispersion-liquid 100 section next (NeoRad NR-440 (trade name)) The Zeneka [Co.] make, 40% (underwater) of resinous principles, the acid number (before neutralization): What dissolved about 25 and the weight-average-molecular-weight:7200 (henceforth NeoRad NR-440) 18.8 section in the acetone 30 section was dropped, it agitated for 40 minutes at 30 degrees C the back, the watercolor pigment dispersing element was obtained (the 2nd process), the mean particle diameter of a particulate material was measured, and a water resisting property and solvent resistance were evaluated further.

[0060] A result is shown in Table 1.

[0061] Said approach estimated a water resisting property and solvent resistance using the dispersion liquid obtained at the 1st process of example of comparison 1 example 1.

[0062] A result is shown in Table 1.

[0063] The ammonia neutralization object (neutralization index: 105%) of the example 2 red pigment (pigment red 22 diameter of primary particle: 0.06 micrometers) 25 section, and the styrene-alpha-methyl-styrene-acrylic-acid copolymer (alpha-methyl-styrene [styrene / /] acrylic acid (weight ratio): 30/25/45, acid-number:234, weight-average-molecular-weight:9000) 6.3 section, the glycerol 5 section, the antiseptics 0.1 section, and ion exchange water About the watercolor pigment constituent adjusted in addition so that solid content concentration might become 30%, wet-grinding equipment was operated so that the residence time might become 15 minutes, dispersion liquid were obtained (the 1st process), and the mean particle diameter of a particulate material was measured.

[0064] Having kept the temperature of a system at 30 degrees C, and agitating said dispersion-liquid 100 section next, what dissolved the NeoRad NR-440 20 section in the acetone 30 section was dropped, it agitated for 40 minutes at 30 degrees C the back, the watercolor pigment dispersing element was obtained (the 2nd process), the mean particle diameter of a particulate material was measured, and a water resisting property and solvent resistance were evaluated further.

[0065] A result is shown in Table 1.

[0066] Changed into benzene the acetone of the water soluble solvent used at the 2nd process of example of comparison 2 example 2, and benzene was removed by the separating funnel after the 2nd process termination, and also the watercolor pigment dispersing element was obtained like the

example 2, the mean particle diameter of a particulate material was measured, and a water resisting property and solvent resistance were evaluated further.

[0067] A result is shown in Table 1.

[0068] The ammonia neutralization object (neutralization index: 107%) of the example 3 blue pigment (pigment blue 15:6 diameter of primary particle: 0.06 micrometers) 24 section, and the styrene-maleic-acid copolymer (styrene [✓] maleic acid (weight ratio): 60/40, acid-number:190, weight-average-molecular-weight:3000) 8.5 section, the glycerol 5 section, the antiseptics 0.1 section, and ion exchange water About the watercolor pigment constituent adjusted in addition so that solid content concentration might become 30%, wet-grinding equipment was operated so that the residence time might become 15 minutes, dispersion liquid were obtained (the 1st process), and the mean particle diameter of a particulate material was measured.

[0069] Having kept the temperature of a system at 30 degrees C, and agitating said dispersion-liquid 100 section next, what dissolved the NeoRad NR-440 19 section in the acetone 30 section was dropped, it agitated for 40 minutes at 30 degrees C the back, the watercolor pigment dispersing element was obtained (the 2nd process), the mean particle diameter of a particulate material was measured, and a water resisting property and solvent resistance were evaluated further.

[0070] A result is shown in Table 1.

[0071] The self-emulsification mold resin used at the 2nd process of example of comparison 3 example 3 was changed into NeoRez R-960 (trade name) (the Zeneka [Co.] make, the acid number: about 20, weight-average-molecular-weight:300000-700000) from NeoRad NR-440, and also the watercolor pigment dispersing element was obtained like the example 3, the mean particle diameter of a particulate material was measured, and a water resisting property and solvent resistance were evaluated further.

[0072] A result is shown in Table 1.

[0073] The ammonia neutralization object (neutralization index: 108%) of the example 4 green pigment (pigment Green 7 diameter of primary particle: 0.05 micrometers) 25 section, and the styrene-methacrylic-acid copolymer (styrene [✓] methacrylic acid (weight ratio): 65/35, acid-number:170, weight-average-molecular-weight:8500) 8.8 section, the glycerol 5 section, the antiseptics 0.1 section, and ion exchange water About the watercolor pigment constituent adjusted in addition so that solid content concentration might become 30%, wet-grinding equipment was operated so that the residence time might become 15 minutes, dispersion liquid were obtained (the 1st process), and the mean particle diameter of a particulate material was measured.

[0074] Having kept the temperature of a system at 30 degrees C, and agitating said dispersion-liquid 100 section next, what dissolved the NeoRad NR-440 19 section in the acetone 30 section was dropped, it agitated for 40 minutes at 30 degrees C the back, the watercolor pigment dispersing element was obtained (the 2nd process), the mean particle diameter of a particulate material was measured, and a water resisting property and solvent resistance were evaluated further.

[0075] A result is shown in Table 1.

[0076] The water-soluble resin used at the 1st process of example of comparison 4 example 4 was changed into NeoRad NR-440 from the styrene-methacrylic-acid copolymer, and also the 1st process as well as an example 4 was performed, dispersion liquid were obtained, the mean particle diameter of a particulate material was measured, and a water resisting property and solvent resistance were evaluated further.

[0077] A result is shown in Table 1.

[0078]

[Table 1]

	第1工程分散液	水性顔料分散体		
	平均粒子径 (nm)	平均粒子径	耐水性	耐溶剂性
实施例1	132	135	○	○
比较例1	132	—	△	×
实施例2	113	117	○	○
比较例2	113	210	×	×
实施例3	125	130	○	○
比较例3	125	200	○	△
实施例4	117	120	○	○
比较例4	190	—	△	△

[0079] The result shown in Table 1 shows not ****(ing) the watercolor pigment dispersing element of the examples 1-4 acquired by the process of this invention, even if distribution of the 1st process is easy and trickles self-emulsification mold resin at the 2nd process, and excelling in a water resisting property and solvent resistance.

[0080] It is inferior by the water resisting property and solvent resistance with the dispersion liquid of the example 1 of a comparison acquired on the other hand by the manufacture approach of only the 1st process which used conventional water-soluble resin. Moreover, in the example 2 of a comparison which used the solvent with small compatibility to water, and the example 3 of a comparison which used self-emulsification mold resin with large weight average molecular weight, when self-emulsification mold resin is dropped at the 2nd process, a **** inclination is seen. Furthermore, in the 1st process, it turns out that atomization is difficult in the example 4 of a comparison which self-emulsification mold resin was used [example] instead of water-soluble resin, and distributed the pigment.

[0081]

[Effect of the Invention] According to the process of this invention, the watercolor pigment dispersing element which was excellent in preservation stability, a water resisting property, and solvent resistance with the particle can be easily manufactured only by adding one process to the conventional approach in a short time.

[0082] Moreover, since it is what has a property like the above, the watercolor pigment dispersing element obtained by the process of this invention can be suitably used also in the field as which high physical properties are required in respect of the hue of a water paint, printing ink, copying ink, and not only textile printing but a color filter, the ink for ink jets, etc., tinting strength, and transparency.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the manufacture approach of a watercolor pigment dispersing element useful to a water paint, water color ink, textile printing or a color filter, the toner for ink jets, etc.

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EFFECT OF THE INVENTION

[Effect of the Invention] According to the process of this invention, the watercolor pigment dispersing element which was excellent in preservation stability, a water resisting property, and solvent resistance with the particle can be easily manufactured only by adding one process to the conventional approach in a short time.

[0082] Moreover, since it is what has a property like the above, the watercolor pigment dispersing element obtained by the process of this invention can be suitably used also in the field as which high physical properties are required in respect of the hue of a water paint, printing ink, copying ink, and not only textile printing but a color filter, the ink for ink jets, etc., tinting strength, and transparency.

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TECHNICAL PROBLEM

[Description of the Prior Art] From the former, the pigment dispersing element has been broadly used for applications, such as a coating, printing ink, writing-materials ink, and textile printing. And an application is being expanded to the object for ink jets, or color filters, therefore recent years require the improvement in the engine performance of a pigment dispersing element.

[0003] Generally a water pigment dispersing element is stabilized by a non-ion-operation or ion-operation.

[0004] A hydrophobic part adsorbs with a pigment, a hydrophilic part extends underwater, and the nonionic surfactant or water soluble resin stabilized according to a non-ion-operation prevents the re-condensation between pigment particles entropy-wise or in three dimensions.

[0005] Moreover, in the case of the cationic surfactant stabilized according to an ion-operation, an anionic detergent, or neutralization mold resin, by ionizing first, the part in which a hydrophilic property appears extends underwater, and an electric double layer is formed in the perimeter of a pigment particle. And this electric double layer induces electric repulsive force, and prevents the re-condensation between pigment particles.

[0006] As for the watercolor pigment dispersing element currently distributed by such stabilization device, various problems appear by the application. For example, the coating which used the pigment dispersing element distributed using the surfactant has the problem that the water resisting property of the paint film obtained is bad. Moreover, since the pigment and the dispersant are paying well only by weak coupling called adsorption, a general pigment dispersing element has the problem that solvent resistance is weak, weakly that is, in the polar change in a water medium.

[0007] This invention is made in view of said conventional technique, and aims at offering the manufacture approach of a watercolor pigment dispersing element of having excelled in preservation stability, a water resisting property, and solvent resistance by the particle.

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MEANS

[Means for Solving the Problem] this invention persons came to complete this invention, as a result of repeating examination wholeheartedly in order to obtain the watercolor pigment dispersing element which was excellent in preservation stability, a water resisting property, and solvent resistance with the particle.

[0009] that is, this invention makes a water medium distribute (1) pigment beforehand using a surfactant and (or) water-soluble resin — the 1st process (2) The dispersion liquid obtained at the 1st process and the liquid made to dissolve the self-emulsification mold resin which has weight average molecular weight in the range of 3000-100000 in a water soluble solvent are mixed. The manufacture approach of the watercolor pigment dispersing element which consists of the 2nd process which makes a pigment front face fix self-emulsification mold resin (claim 1), (1) — a water medium is made to distribute a pigment beforehand using a surfactant and (or) water-soluble resin — the 1st process (2) The liquid made to dissolve the self-emulsification mold resin and the cross linking agent which have the dispersion liquid obtained at the 1st process and weight average molecular weight in the range of 3000-100000 in a water soluble solvent is mixed. The manufacture approach of the watercolor pigment dispersing element which consists of the 2nd process which makes a pigment front face fix self-emulsification mold resin and a cross linking agent (claim 2), the manufacture approach (claim 3) according to claim 1 or 2 that said surfactants are a nonionic surfactant and (or) an anionic detergent — Said water-soluble resin has at least one sort of hydrophilic radicals of a carboxyl group and a sulfonic group in a molecule. a styrene unit and (or) a methyl styrene unit 50% of the weight The manufacture approach according to claim 1 or 2 that the weight average molecular weight contained above is the polymer of 2000-20000 (claim 4), (It is hereafter called %) It is related with the manufacture approach (claim 5) according to claim 1 or 2 that said self-emulsification mold resin is urethane system resin or acrylic resin, and the manufacture approach (claim 6) according to claim 1, 2, or 5 which has the acid number of said self-emulsification mold resin in the range of 20-110.

[0010]

[Embodiment of the Invention] a pigment is made to distribute beforehand first in this invention, using a surfactant and (or) water-soluble resin as the 1st process by the water medium At this time, as long as it is required, other additives may also be added beforehand.

[0011] There is especially no limitation in said pigment, for example, various inorganic pigments, such as oxide; cadmium yellow, such as various organic pigments, such as polycyclic type pigment; color chelates, such as azo pigment; phthalocyanine pigments, such as an azo lake, insoluble azo pigment, a disazo condensation pigment, and a chelate azo pigment, a perylene pigment, a thioindigo pigment, an isoindolinone pigment, and a kino FUTARON pigment, and titanium oxide, red ocher, chromic oxide, iron black, Chrome Vermilion, Berlin blue, ultramarine blue, and Synthetic Ochre, carbon black, etc. are raised. These may be used independently and may be used combining two or more sorts.

[0012] As an example of said organic pigment, for example The PIKUMENTO yellow 1 (C. I.11680), The pigment yellow 3 (C. I.11710), the pigment yellow 74 (C. I.11741), The pigment yellow 83 (C. I.21108), the pigment yellow 106, the pigment yellow 108 (C. I.68240), The pigment yellow 117, the pigment yellow 126, the pigment yellow 139, the pigment yellow 185, pigment Orange 5 (C. I.12075), Pigment Orange 67, the pigment red 3 (C. I.12120), The pigment red 22 (C. I.12315), the pigment red

48:1 (C. I.15865:1), The pigment red 48:4 (C. I.15865:4), the pigment red 101 (C. I.77491), The pigment red 112 (C. I.12370), the pigment red 123 (C. I.71145), The pigment red 169 (C. I.45160:2), the pigment violet 23 (C. I.51319), The pigment violet 27 (C. I.42555:3), the pigment blue 1 (C. I.42595:3), The pigment blue 15:1 (C. I.74160), the pigment blue 15:3 (C. I.74160), The pigment blue 15:6 (C. I.74160), the pigment blue 61 (C. I.42765:1), pigment Green 7 (C. I.74260), pigment Green 36 (C. I.74265), etc. are raised.

[0013] Moreover, the pigment yellow 42 (C. I.77492), pigment White 6 (C. I.77981), the pigment blue 27 (C. I.77510), the pigment blue 29 (C. I.77007), the pigment black 7 (C. I.77266), etc. are raised as an example of said inorganic pigment.

[0014] In addition, you may be any, such as what there is no limitation especially in the gestalt of said pigment, and performed various surface treatment, fine particles, and an aqueous paste. These may be used independently and may be used combining or more 2 kind. Among these, the point that dispersibility is good to an aqueous paste is desirable.

[0015] Moreover, when dispersibility is taken into consideration, as for the primary particle diameter of said pigment, it is desirable that they are usually about 0.1 micrometers or less and 0.01–0.06 micrometers of *****.

[0016] It is desirable to adjust so that it may become 80% or less and 40% or less of *****, since it becomes the cause by which a diffusion rate becomes slow in case it will mix with a water soluble solvent at the 2nd process, if it is desirable to adjust so that the concentration in the dispersion liquid obtained at the 1st process in order to obtain sufficient tinting strength, although there is especially no limitation in the loadings of said pigment may become 1% or more and 3% or more of ***** and the viscosity of dispersion liquid is too high, and particle diameter becomes large.

[0017] as long as it has been used from the former as said surfactant and (or) water-soluble resin, there is especially no limitation. For example, water-soluble resin, such as surfactants, such as a cationic surfactant, an anionic detergent, and a nonionic surfactant, and water-soluble acrylic resin, water-soluble nylon system resin, water-soluble epoxy system resin, water-soluble naturally-occurring polymers, is raised. these — independent — business — you may use with a sufficient potato combining two or more sorts. That is, since distribution of the 1st process is the same as the process of the conventional watercolor pigment dispersing element, it has the merit which the conventional manufacturing facility can use as it is.

[0018] As a nonionic surfactant of said surface active agents, the nonionic surfactant of polyoxyethylene alkyl ether, polyoxyethylene alkyl aryl ether, a polyoxyethylene oxypropylene block copolymer, a sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, polyoxyethylene sorbitol fatty acid ester, a glycerine fatty acid ester, polyoxyethylene fatty acid ester, polyoxyethylene alkylamine, and a fluorine system, the nonionic surfactant of a silicone system, etc. are raised. These may be used independently and may be used combining or more 2 kind.

[0019] As an anionic detergent of said surfactants, a fatty-acid salt, an alkyl-sulfuric-acid ester salt, alkylaryl sulfonates, alkyl naphthalenesulfonate, a dialkyl sulfonate, dialkyl sulfo succinate, alkyl diaryl ether disulfon acid chloride, alkyl phosphate, a polyoxyethylene-alkyl-ether sulfate, a polyoxyethylene-alkyl-aryl-ether sulfate, a naphthalene sulfonic-acid formalin condensate, polyoxyethylene alkyl phosphate, a glycerol borate fatty-acid-ester salt, etc. are raised. These may be used independently and may be used combining or more 2 kind.

[0020] As a cationic surfactant of said surfactants, alkylamine salt, quarternary ammonium salt, sulfonium salt, phosphonium salt, etc. are raised. These may be used independently and may be used combining two or more sorts.

[0021] Although there is no limitation especially in the amount of said surfactant used, in order to fully raise the dispersibility of the pigment in the dispersion liquid of the 1st process If it is desirable that they are the 5 or more sections and the 10 or more section of ***** and it considers adding self-emulsification mold resin further at the 2nd process to said pigment 100 weight section (henceforth the section), so that the viscosity of dispersion liquid may not go up too much And in order for a surfactant to enter too much superfluously and to make it quality not worsen, it is desirable that they are the 100 or less sections and the 50 or less section of *****.

[0022] Said water-soluble resin is what is used in order to distribute a pigment. Although there is

especially no limitation in the class, improve the balance of the hydrophobic group which sticks to a pigment, and the hydrophilic group developed in a water medium, and the dispersion effect of water-soluble resin is heightened. hydrophobic monomeric units, such as for example, a styrene unit from the point of raising dispersibility, and a methyl styrene unit, — water-soluble resin of 55 – 70% of ***** is preferably desirable 50% or more and further 50 to 70% in a styrene unit and (or) a methyl styrene unit. Moreover, when improvement in dispersibility is taken into consideration, as for the weight average molecular weight of this water-soluble resin, it is desirable that they are 2000–20000, and ***** 2500–15000.

[0023] That to which the acid number which neutralizes with an alkaline compound and presents water solubility as said water-soluble resin neutralized the resin of 115–300, and ***** 150–250 with the alkaline compound to 110–300, and a pan is desirable. Therefore, the polymer which has in a molecule at least one sort of hydrophilic radicals, such as an amount which serves as this acid number, for example, a carboxyl group, and a sulfonic group, is desirable.

[0024] as the water-soluble resin used for this invention from the above thing — the inside of a molecule — at least one sort of hydrophilic radicals, such as a carboxyl group and a sulfonic group, — the acid number — 110–300 — further — the thing of 2000–20000, and ***** 2500–15000 has the desirable weight average molecular weight which has so that it may become 115–300, and ***** 150–250, and contains a styrene unit and (or) a methyl styrene unit 55 – 70% of ***** 50% or more.

[0025] As an example of said water-soluble resin, for example A styrene-acrylic-acid copolymer, A styrene-methyl styrene-acrylic-acid copolymer, styrene-acrylic-acid-acrylic ester (in addition with said ester) Like the following which says with a carbon number of about one to four low-grade alkyl ester, a copolymer, ;, for example, styrene-maleic-acid copolymers, such as a styrene-methacrylic-acid copolymer and a styrene-methacrylic-acid-acrylic ester copolymer, A styrene-methyl styrene-maleic-acid copolymer, a styrene-acrylic ester-maleic-acid copolymer, ;, for example, styrene-acrylic ester-styrene sulfonic-acid copolymers, such as a styrene-methacrylic ester-maleic-acid copolymer, What used the styrene-methacrylic sulfonic-acid copolymer, the styrene-acrylic ester-allyl compound sulfonic-acid copolymer, etc. as sodium salt, potassium salt, ammonium salt, etc. is raised. These may be used independently and may be used combining two or more sorts.

[0026] Although there is no limitation especially in said alkaline compound, alkali-metal salts, such as organic amines; sodium hydroxides, such as ammonia; monoethanolamine and a morpholine, a potassium hydroxide, and a lithium hydroxide, etc. are useful, for example. These may be used independently and may be used combining two or more sorts.

[0027] formula (I) from the point that it is desirable that it is the amount by which the carboxyl group contained in said water-soluble resin, a sulfonic group, etc. can be neutralized as for the addition of said alkaline compound: neutralization-index (%) = -- [(equivalent of the added alkaline compound) — / (acid equivalent of resin)]x100 (I)

It is desirable that it is the amount from which it is based [(the acid equivalent of resin is calculated among a formula from the acid number of the resin which turns into water-soluble resin by neutralization), and], and the computed neutralization index serves as 90 – 120% of ***** 80 to 150%.

[0028] moreover, in case neutralization of water-soluble resin with said alkaline compound neutralizes the resin which serves as a dispersant by neutralization and makes it dissolve in water and (or) an organic solvent, it is desirable to carry out from the point that the dissolution is promoted further, by heating to 50 degrees C or more and the temperature of 70–90 degree C of *****.

[0029] Although there is especially no limitation in the amount of said water-soluble resin used, in order to fully raise the dispersibility of the pigment in the dispersion liquid of the 1st process If it is desirable that they are the 5 or more sections and the 10 or more section of ***** and it considers adding self-emulsification mold resin further at the 2nd process to said pigment 100 section, so that the viscosity of dispersion liquid may not rise too much And in order for a dispersant to enter too much superfluously and to make it quality not worsen, it is desirable that they are the 100 or less sections and the 50 or less section of *****.

[0030] There is no limitation especially in the water medium used for the dispersion liquid of said 1st process, for example, ion exchange water, distilled water, purified water, etc. are raised. moreover, the

amount of the water of dispersion liquid — for example, it is good at the residue of said pigment, a surfactant, and (or) water-soluble resin (henceforth a dispersant), and good in an amount from which the solid content (pigment, dispersant) concentration of dispersion liquid usually serves as 10 – 40% of ***** about 4 to 90%.

[0031] At the 1st process, as long as it is required, other additives may be added in the range which does not spoil the effectiveness of this invention.

[0032] As said additive, for the purpose of improvement in the various physical properties of the watercolor pigment dispersing element finally obtained etc., it is used, for example, additives, such as antiseptics, an antifungal agent, a defoaming agent, an ultraviolet ray absorbent, and a stabilizer, a part of water soluble solvent mentioned later, a saccharide, etc. are raised.

[0033] what is necessary is just to prepare dispersion liquid by the approach as usual at the 1st process that what is necessary is just to be able to make a water medium distribute a pigment beforehand using a surfactant and (or) water-soluble resin for example, if required, other additives will be mixed, and it is carried out a pigment, a surfactant and (or) water-soluble resin, a water medium, and by operating grinding equipments, such as wet-grinding equipment, so that the residence time may become 3 – 150 minutes. Here, the residence time means the scale showing how much liquid had stopped into grinding equipment.

[0034] Next, if required, the dispersion liquid obtained at the 1st process, self-emulsification mold resin, and the liquid made to dissolve a cross linking agent in a water soluble solvent will be mixed, and self-emulsification mold resin will be made to fix as the 2nd process by the pigment front face.

[0035] Although said self-emulsification mold resin carries out self-distribution without an emulsifier into a water medium, it dissolves this in a water soluble solvent once. it is thought that the surfactant and (or) water-soluble resin which were used at the 1st process are emitted by mixing of a water soluble solvent from a pigment front face while it deposits sticking to self-emulsification mold resin on a pigment front face, when this solution is mixed with the dispersion liquid obtained at the 1st process.

[0036] Thus, since it is as strong as association with the pigment of a watercolor pigment dispersing element and self-emulsification mold resin which are formed does not become a thing compared with association by general adsorption, it is thought that solvent resistance improves remarkably.

Moreover, since compatibility [as opposed to water in self-emulsification mold resin itself] is small compared with water-soluble resin, waterproof improvement is also expected.

[0037] Although there is especially no limitation in said self-emulsification mold resin, when an alkaline compound neutralizes, for example, the resin of 20–110, and ***** 20–80 is preferably used for the acid number which presents self-dispersibility. Therefore, the polymer which has in a molecule at least one sort of hydrophilic radicals, such as an amount which serves as this acid number, for example, a carboxyl group, and a sulfonic group, especially a carboxyl group is desirable. If pigment particle diameter becomes large, the inclination for the preservation stability of a watercolor pigment dispersing element to disadvantage-crack-come to be easy arises and 110 is surpassed when the acid number of said self-emulsification mold resin was lower than 20 and it is made to mix with dispersion liquid at the 2nd process, the solubility to water will become large and the inclination it to become impossible that it is hard to expect a water resisting property and solvent resistance will arise.

[0038] If it is desirable that they are 3000–100000, and ***** 5000–50000 as for the weight average molecular weight of said self-emulsification mold resin and it is lower than 3000, improvement in the water resisting property of a watercolor pigment dispersing element and solvent resistance is not expectable, and when 100000 was surpassed and it is made to mix at the 2nd process, a pigment particle becomes easy to become large.

[0039] As an example of said self-emulsification mold resin, such mixture, such as polyvinyl system resin; urethane system resin, such as acrylic-acid system resin [, such as acrylic resin of thermoplasticity, thermosetting, or denaturation and polyacrylamide,], for example, polyvinyl alcohol, polyvinyl acetate, vinyl chloride system resin, and a polyvinyl butyral, polyether system resin, epoxy system resin, fluorine system resin, and silicone system resin, is raised, for example. Among these, urethane system resin and acrylic resin are desirable from the point of film formation nature and the safety to membranous reinforcement and the membranous body.

[0040] you may be any, such as a thing which there is no limitation especially in the gestalt of said self-emulsification mold resin, for example, was distributed in fine particles, water, and (or) a water soluble solvent, or a liquefied object in which it was made to dissolve. In addition, what is necessary is just to adjust the amount of said water medium in accordance with the amount of the water contained or a water soluble solvent, when water and a water soluble solvent are included.

[0041] In order to fully raise a water resisting property and solvent resistance, although there is especially no limitation in the amount of the net (solid content) used of said self-emulsification mold resin, it is desirable [it is desirable that they are the 5 or more sections and the 10 or more section of ***** to said pigment 100 section, and] that they are the 100 or less sections and the 60 or less section of ***** so that self-emulsification mold resin is mixed in large quantities, pigment particle diameter may not be enlarged or viscosity may not rise too much.

[0042] In addition, since this resin works on a pigment front face as a dispersant after self-emulsification mold resin's fixing, after making it neutralize self-emulsification mold resin in a water soluble solvent, it is necessary to mix.

[0043] Although there is especially no limitation in the neutralizer of said self-emulsification mold resin, alkali-metal hydroxides, such as organic amines; sodium hydroxides, such as ammonia; monoethanolamine, diethanolamine, triethanolamine, and a morpholine, a potassium hydroxide, and a lithium hydroxide, etc. are common, for example. These may be used independently and may be used combining two or more sorts.

[0044] As for the addition of said neutralizer, it is desirable that it is the amount to which the neutralization index computed based on the formula (I) becomes 90 - 120% of ***** from the point that it is desirable that it is the amount by which the carboxyl group contained in said self-emulsification mold resin, a sulfonic group, etc. can be neutralized, 80 to 150%.

[0045] Said cross linking agent is used in order to raise a water resisting property and solvent resistance further, and it should just choose what was suitable suitably according to the class of self-emulsification mold resin. For example, when self-emulsification mold resin contains the carboxyl group and the epoxy resin and the poly aziridine compound contain the hydroxyl group, melamine resin, a urea-resin, the resin that has an isocyanate radical are raised.

[0046] Although what is necessary is just to use the amount for which the amount of said cross linking agent used was also suitable suitably according to the class of self-emulsification mold resin, generally it is the five to 18 section above all the three to 35 section to the self-emulsification mold resin 100 net section.

[0047] Said water soluble solvent is 20 degrees C, and it is a water soluble solvent free mixable with water. Although there will be especially no limit in the class if said self-emulsification mold resin is dissolved For example, an acetone; The methanol of alcohols, ethanol, n-propanol, Isopropanol etc.; The ethylene glycol of glycols, propylene glycol, ; glycerols, such as a diethylene glycol, dipropylene glycol, and tetraethylene glycol; Diethylene-glycol diethylether of the ether of polyhydric alcohol, The diethylene-glycol monobutyl ether, ethylene glycol monoethyl ether, Ethylene glycol monobutyl ether, methyl carbitol, ethyl carbitol, Butyl carbitol, the triethylene glycol monomethyl ether, Triethanolamine of; ** nitrogen compounds, such as the triethylene glycol monoethyl ether and propylene glycol monomethyl ether, etc.; the expenses [degrees C /, such as dimethyl sulfoxide, / 20] of a thing free mixable with water are covered. These may be used independently and may be used combining two or more sorts. Among these, self-emulsification mold resin is often melted, the boiling point is lower than water, and the acetone from the point that diffusion is smoothly performed by mixing with the dispersion liquid of the 1st process, ethanol, etc. are desirable.

[0048] Although there is especially no limit in the amount of said water soluble solvent used, when dissolving said self-emulsification mold resin, in order for it to enter too much that they are the 100 or more sections and the 150 or more section of ***** preferably and superfluously and to make it quality not worsen [as opposed to / in order to make it the viscosity not become not much high / the self-emulsification mold resin 100 net section], it is desirable that they are the 15000 or less sections and the 10000 or less section of *****.

[0049] At the 2nd process, that what is necessary is just to be able to make a pigment front face fix self-emulsification mold resin, although there is especially no limitation, if required, the dispersion liquid obtained, for example at the 1st process, self-emulsification mold resin, and the liquid made to

dissolve a cross linking agent in a water soluble solvent will be mixed, and it is carried out by agitating for 30 - 60 minutes.

[0050] Although mixing at the time of mixing the dispersion liquid obtained at the 1st process and the solution in which self-emulsification mold resin etc. was dissolved carries out and it changes as a direction with classes of the solid content concentration of said dispersion liquid and viscosity, the self-emulsification mold resin concentration of said solution and viscosity, and water soluble solvent etc., the thing which is fully a line about churning and which is made for either to be dropped without moving from its seat is desirable so that said dispersion liquid or said solution may diffuse quickly again enough. Moreover, as for the volume ratio of said dispersion liquid in the case of mixing, and said solution, it is desirable from the point of the stability of a watercolor pigment dispersing element that it is $98 / 2 - 66/34$. Furthermore, it is desirable that it is beyond a room temperature as temperature in the case of making it mix at temperature lower about 20 degrees C than the boiling point of a water soluble solvent.

[0051] Into said solution, when the cross linking agent is added, after mixing both liquid, it is suitable conditions, and heating churning may be carried out and crosslinking reaction may be advanced. Moreover, depending on an application, the water soluble solvent in a watercolor pigment dispersing element is also removable with distillation.

[0052] Thus, by making a pigment front face fix self-emulsification mold resin, the watercolor pigment dispersing element manufactured demonstrates the outstanding water resisting property and solvent resistance.

[Translation done.]

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EXAMPLE

[Example] Hereafter, although the effectiveness of the manufacture approach of this invention is further shown in a detail based on an example, of course, this invention is not limited to these.

[0054] In addition, the evaluation approach used in the following examples and examples of a comparison is shown collectively below.

[0055] (Measurement of mean particle diameter) Predetermined dispersion liquid or a predetermined watercolor pigment dispersing element is diluted with ion exchange water so that pigment concentration may serve as 0.1 g/l, and the mean particle diameter of a particulate material is measured using this diluent by micro truck UPA by Leeds - and - North lap company.

[0056] (Water resisting property) After carrying out drawdown of predetermined dispersion liquid or a predetermined watercolor pigment dispersing element to an OHP sheet by the 1.5-mil applicator and drying it for 10 minutes at 125 degrees C, it is immersed in water for 3 minutes, the existence of a blot of a color is judged visually, and the following criteria estimate.

O : — a blot of a color — there is nothing — good thing **: — thing x: in which slight abnormalities (blot of a color) were accepted — what the abnormalities (blot of a color) which are not desirable were accepted in [0057] (Solvent resistance) After carrying out drawdown of predetermined dispersion liquid or a predetermined watercolor pigment dispersing element to an OHP sheet by the 1.5-mil applicator and drying it for 10 minutes at 125 degrees C, it is immersed in a solvent (ethanol/water (weight ratio): 1/1) for 3 minutes, the existence of a blot of a color is judged visually, and it evaluates according to a water resisting property.

[0058] The ammonia neutralization object (neutralization index: 110%) of the example 1 yellow pigment (pigment yellow 83 diameter of primary particle: 0.04 micrometers) 25 section, and the styrene-acrylic-acid copolymer (styrene [] acrylic acid (weight ratio): 70/30, acid-number: 170, weight-average-molecular-weight: 12000) 5 section, the glycerol 5 section, the antiseptics (best side - 1177A (Dainippon Ink & Chemicals, Inc. make)) (henceforth antiseptics) 0.1 section, and ion exchange water. About the watercolor pigment constituent adjusted in addition so that solid content concentration might become 30%, wet-grinding equipment was operated so that the residence time might become 15 minutes, dispersion liquid were obtained (the 1st process), and the mean particle diameter of a particulate material was measured.

[0059] The urethane system resin emulsion which is self-emulsification mold resin while keeping the temperature of a system at 30 degrees C and agitating said dispersion-liquid 100 section next (NeoRad NR-440 (trade name)) The Zeneka [Co.] make, 40% (underwater) of resinous principles, the acid number (before neutralization): What dissolved about 25 and the weight-average-molecular-weight: 7200 (henceforth NeoRad NR-440) 18.8 section in the acetone 30 section was dropped, it agitated for 40 minutes at 30 degrees C the back, the watercolor pigment dispersing element was obtained (the 2nd process), the mean particle diameter of a particulate material was measured, and a water resisting property and solvent resistance were evaluated further.

[0060] A result is shown in Table 1.

[0061] Said approach estimated a water resisting property and solvent resistance using the dispersion liquid obtained at the 1st process of example of comparison 1 example 1.

[0062] A result is shown in Table 1.

[0063] The ammonia neutralization object (neutralization index: 105%) of the example 2 red pigment

[0076] The water-soluble resin used at the 1st process of example of comparison 4 example 4 was changed into NeoRad NR-440 from the styrene-methacrylic-acid copolymer, and also the 1st process as well as an example 4 was performed, dispersion liquid were obtained, the mean particle diameter of a particulate material was measured, and a water resisting property and solvent resistance were evaluated further.

[0077] A result is shown in Table 1.

[0078]

[Table 1]

表 1

	第 1 工程分散液	水性顔料分散体		
	平均粒子径 (nm)	平均粒子径	耐水性	耐溶剤性
実施例 1	132	135	○	○
比較例 1	132	—	△	×
実施例 2	113	117	○	○
比較例 2	113	210	×	×
実施例 3	125	130	○	○
比較例 3	125	200	○	△
実施例 4	117	120	○	○
比較例 4	190	—	△	△

[0079] The result shown in Table 1 shows not ****(ing) the watercolor pigment dispersing element of the examples 1-4 acquired by the process of this invention, even if distribution of the 1st process is easy and trickles self-emulsification mold resin at the 2nd process, and excelling in a water resisting property and solvent resistance.

[0080] It is inferior by the water resisting property and solvent resistance with the dispersion liquid of the example 1 of a comparison acquired on the other hand by the manufacture approach of only the 1st process which used conventional water-soluble resin. Moreover, in the example 2 of a comparison which used the solvent with small compatibility to water, and the example 3 of a comparison which used self-emulsification mold resin with large weight average molecular weight, when self-emulsification mold resin is dropped at the 2nd process, a **** inclination is seen. Furthermore, in the 1st process, it turns out that atomization is difficult in the example 4 of a comparison which self-emulsification mold resin was used [example] instead of water-soluble resin, and distributed the pigment.

[Translation done.]

(pigment red 22 diameter of primary particle: 0.06 micrometers) 25 section, and the styrene-alpha-methyl-styrene-acrylic-acid copolymer (alpha-methyl-styrene [styrene / / /] acrylic acid (weight ratio): 30/25/45, acid-number:234, weight-average-molecular-weight:9000) 6.3 section, the glycerol 5 section, the antiseptics 0.1 section, and ion exchange water About the watercolor pigment constituent adjusted in addition so that solid content concentration might become 30%, wet-grinding equipment was operated so that the residence time might become 15 minutes, dispersion liquid were obtained (the 1st process), and the mean particle diameter of a particulate material was measured. [0064] Having kept the temperature of a system at 30 degrees C, and agitating said dispersion-liquid 100 section next, what dissolved the NeoRad NR-440 20 section in the acetone 30 section was dropped, it agitated for 40 minutes at 30 degrees C the back, the watercolor pigment dispersing element was obtained (the 2nd process), the mean particle diameter of a particulate material was measured, and a water resisting property and solvent resistance were evaluated further.

[0065] A result is shown in Table 1.

[0066] Changed into benzene the acetone of the water soluble solvent used at the 2nd process of example of comparison 2 example 2, and benzene was removed by the separating funnel after the 2nd process termination, and also the watercolor pigment dispersing element was obtained like the example 2, the mean particle diameter of a particulate material was measured, and a water resisting property and solvent resistance were evaluated further.

[0067] A result is shown in Table 1.

[0068] The ammonia neutralization object (neutralization index: 107%) of the example 3 blue pigment (pigment blue 15:6 diameter of primary particle: 0.06 micrometers) 24 section, and the styrene-maleic-acid copolymer (styrene [/] maleic acid (weight ratio): 60/40, acid-number:190, weight-average-molecular-weight:3000) 8.5 section, the glycerol 5 section, the antiseptics 0.1 section, and ion exchange water About the watercolor pigment constituent adjusted in addition so that solid content concentration might become 30%, wet-grinding equipment was operated so that the residence time might become 15 minutes, dispersion liquid were obtained (the 1st process), and the mean particle diameter of a particulate material was measured.

[0069] Having kept the temperature of a system at 30 degrees C, and agitating said dispersion-liquid 100 section next, what dissolved the NeoRad NR-440 19 section in the acetone 30 section was dropped, it agitated for 40 minutes at 30 degrees C the back, the watercolor pigment dispersing element was obtained (the 2nd process), the mean particle diameter of a particulate material was measured, and a water resisting property and solvent resistance were evaluated further.

[0070] A result is shown in Table 1.

[0071] The self-emulsification mold resin used at the 2nd process of example of comparison 3 example 3 was changed into NeoRez R-960 (trade name) (the Zeneka [Co.] make, the acid number: about 20, weight-average-molecular-weight:300000-700000) from NeoRad NR-440, and also the watercolor pigment dispersing element was obtained like the example 3, the mean particle diameter of a particulate material was measured, and a water resisting property and solvent resistance were evaluated further.

[0072] A result is shown in Table 1.

[0073] The ammonia neutralization object (neutralization index: 108%) of the example 4 green pigment (pigment Green 7 diameter of primary particle: 0.05 micrometers) 25 section, and the styrene-methacrylic-acid copolymer (styrene [/] methacrylic acid (weight ratio): 65/35, acid-number:170, weight-average-molecular-weight:8500) 8.8 section, the glycerol 5 section, the antiseptics 0.1 section, and ion exchange water About the watercolor pigment constituent adjusted in addition so that solid content concentration might become 30%, wet-grinding equipment was operated so that the residence time might become 15 minutes, dispersion liquid were obtained (the 1st process), and the mean particle diameter of a particulate material was measured.

[0074] Having kept the temperature of a system at 30 degrees C, and agitating said dispersion-liquid 100 section next, what dissolved the NeoRad NR-440 19 section in the acetone 30 section was dropped, it agitated for 40 minutes at 30 degrees C the back, the watercolor pigment dispersing element was obtained (the 2nd process), the mean particle diameter of a particulate material was measured, and a water resisting property and solvent resistance were evaluated further.

[0075] A result is shown in Table 1.

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